DETERMINATION OF FLUORINE BY PROTON- INDUCED GAMMA-RAY EMISSION (PIGE) SPECTROMETRY IN IGNEOUS AND METAMORPHIC CHARNOCKITIC ROCKS FROM ROGALAND (S. W. NORWAY)

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More than 200 specimens from different occurrences of the Rogaland igneous complex and surrounding granulite facies metamorphic rocks (S. W. Norway) have been analysed by a direct non-destructive proton induced gamma-ray emission (PIGE) technique. The fluorine contents vary from < 25 ppm to 3500 ppm. There is a good correlation between the concentration of fluorine and that of phosphorus for igneous rocks, suggesting a control of apatite on the F content. In metamorphic rocks, amphibole and biotite besides apatite are the principal cencentrators of fluorine indicating that fluorine in the system is controlled by granulite facies metamorphism conditions.

Introduction

Fluorine is the thirteen element in order of abundance in crustal rocks of the Earth, with an average content of 625 ppm /1/. It is an important constituent of the fluid phase associated with granitic rocks and various mineralizations. Its behaviour in the upper part of the crust, where these rocks generally occur, has been extensively studied /2/. In the deeper part of the crust, it is less well documented. In recent years, its importance has however been emphasized as a possible major constituent besides CO_2 of the fluid phase in equilibrium with igneous and metamorphic rocks of the granulite facies and stressed the need of further geochemical data in these materials.

This paper reports the preliminary data of a geochemical study of fluorine in the granulite facies rocks from the Rogaland Province in S. Norway.

Analytical method

Colorimetry and specific ion-electrode, and to a lesser extent radiochemical neutron activation analysis are commonly used. In all these techniques the samples must be dissolved and chemical elimination of potentially interfering elements must be carried

out, that restricts the analysis of a large number of samples in reasonable time as often required in geochemical studies.

BREWERS and FLACK /3/ were the first to demonstrate that proton induced gamma ray emission (PIGE) spectrometry was capable of measuring fluorine in rock samples. However, the place of the PIGE technique is not yet established in the geosciences and geochemical data by this method are still scarce /4/.

The PIGE technique, currently being developed in Liège University /5/, proved to be valuable for routine fluorine determination ranging from % to ppm levels in geological materials of widely varying compositions including rocks, soils, sediments, minerals and ores /6,7/. The non-destructive PIGE method used here is based on the nuclear reaction

$$^{19}F(p,\alpha\gamma)^{16}O.$$
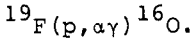
Equipment

The experimental arrangement for PIGE basically consists of three components : a Van de Graaff accelerator, a vacuum irradiation chamber and a detection system with associated electronics for counting the γ rays. It is schematically represented in Fig. 1.
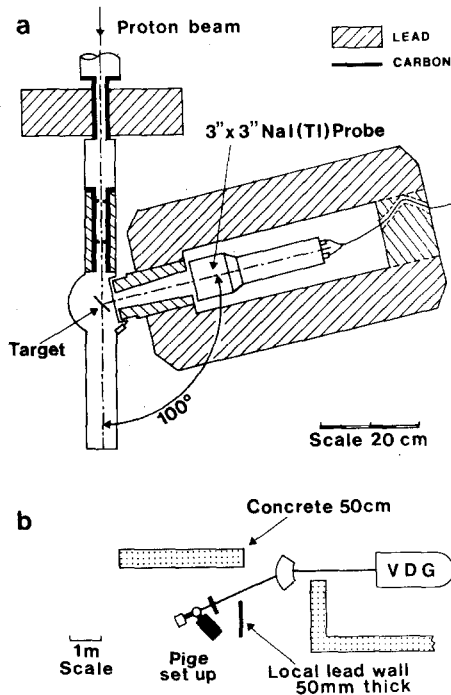

Fig. 1. Schematic diagram of the experimental set-up.

In this work a pellet of geological material mounted on an aluminum target ladder with 16 positions was bombarded in vacuum with a 500 nA beam of 1.5 MeV protons from the 3 MeV Van de Graaff accelerator (HVEC) of the Experimental Nuclear Institute (University of Liège). This bombarding energy was found experimentally to give the best sensitivity. A beam spot area at the sample of about 20 mm^2 was chosen. The emitted γ rays were detected with a 3" x 3" NaI (Tl) gamma probe ($\Delta E/E$ = 7% FWHM) carefully shielded and placed at a distance of 20 cm from the target with a 0.049 sr solid angle at 100° LAB. The resulting pulses were collected in a multichannel height analyser (IN90 Intertechnique) employed for data acquisition and analysis. Each sample required about 45 minutes of running time.

Sample preparation

The powdered rock sample (carefully weighed with a microbalance) was intimately mixed with graphite SP-1C powder (Union Carbide) in a 9:1 weight ratio and regrinded in an agate mortar. The mixture was transferred to a Beckman evacuable die and pressed at 4.10^8Pa in a hydraulic press. A polypropylene film was placed between the pellet and the pressing surface to prevent any contamination and removed afterwards. The resulting pellet which was 13 mm in diameter and 1-2 mm thick proved to be easy to handle. For routine analysis, 200 mg of mixture were prepared (180 mg sample and 20 mg graphite). C acted as a binder and also provided good conduction of the target.

Calibration was effected via primary powder standards. They were fabricated simply by adding known quantities of sodium fluoride (Merck, AR grade purity) to pure quartz (Merck, AR grade purity) and agitating the whole in a Turbula system Schatz for 15 hours to ensure a uniform fluorine distribution. Three replicate pellets from each calibration standard were prepared following the procedure used for the rocks. The γ ray intensity was a linear function of the fluorine content over a wide range of concentrations. "Blank" pellets were made from pure quartz and graphite.

Gamma ray spectrum

A typical example of a gamma spectrum is shown in Fig.2. It is mainly composed by the 7.1 and 6.1 MeV gamma-rays corresponding to the deexcitation of ^{16}O nuclei produced in the reaction ^{19}F$(p,\alpha\gamma)^{16}$O. Due to the pair production phenomenon-important at these energies - five gamma-peaks can be seen corresponding to full energy loss, single escape and double escape. The 6.1 MeV peak was preferred for fluorine analysis because the base line may be more accurately drawn in this gamma spectrum region. For a uniform area sample, the concentration of fluorine can be determined directly from the counts of the gamma ray peak after background corrections and blank contribution subtraction.
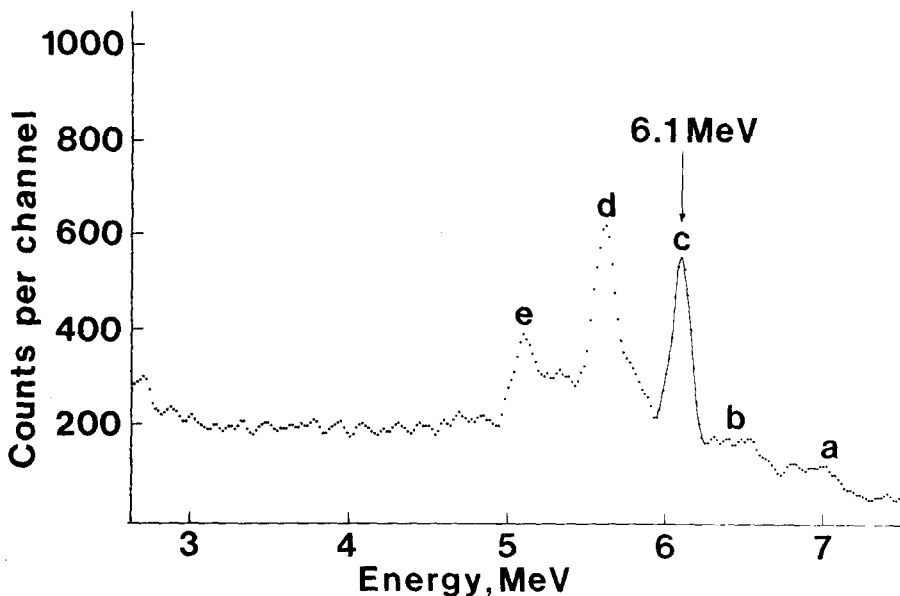
Fig. 2. Typical gamma-ray spectrum; a − 7.1−MeV full-energy peak; b − 7.1−MeV single-escape peak; c − 7.1−
MeV double-escape + 6.1−MeV full-energy peak; d − 6.1−MeV single-escape peak; e − 6.1−MeV
double-escape peak

Limit of detection - Precision - Accuracy

A detailed evaluation of these three parameters which are impor-
tant attributes when judging the merits of a method has been pu-
blished elsewhere /6,7/.
    The limit of detection, defined here as the concentration
corresponding to $3\sqrt{B}$ pulses in the peak (B is the number of pul-
ses in the background), was calculated to be equal to 25 ppm of
fluorine. This low limit of detection is mainly due to a care-
ful study of the gamma shielding of the NaI(Tl) probe. This va-
lue is quite acceptable for most geochemical applications.
    The attained precision was found to be within acceptable
limits:10 % at 100 ppm level, 6 % at 1000 ppm level and 3 % at
1 % concentration level of fluorine. In the present study, dif-
ferent pellets of the granodiorite GSP-1 (U.S.G.S.) were systema-
tically included in every irradiation. The mean value of our
GSP-1 analyses was 3477±195 ppm (n = 48).
    Eighty international geochemical reference samples (GRS)
from different organisms, including igneous, metamorphic and sedi-
mentary silicates,carbonates, phosphates, minerals, soils and
ores have been analysed to check the accuracy of our determina-
tions /6/. Most of our results were within 10 % (or better) of
the quoted values. This accuracy is quite satisfactory especial-
ly considering the range of variation of the available literatu-
re values.

Data

206 igneous and 31 metamorphic rocks from Rogaland were analysed. This province has been extensively studied by P.MICHOT /8/ who unravelled the overall geological history and by many authors who have dealt with geochemical and isotopic aspects (see the review by DUCHESNE et al. /9/).

The igneous rocks

The igneous rocks belong to the anorthosite suite and comprise anorthosite, leuconorite, norite, monzonorite, mangerite, quartz mangerite and charnockite (nomenclature after STRECKEISEN /10/), all members belonging to the charnockitic family.

Contrarily to famous provinces e.g. in the typical region near Madras in India /11/ where charnockites were defined, Rogaland igneous charnockites have not been metamorphosed and thus have preserved their primary magmatic characters and geochemical features.

The igneous rocks are coming from the various geological units of the province. These one essentially comprise
(1) three large massif-type anorthositic bodies essentially made up of anorthosite (more than 90 % of andesine plagioclase) with subordinate amounts of leuconorite and norite
(2) a layered lopolith (the Bjerkreim Sokndal massif) made up of a series of cumulates grading from anorthosite to mangerite and on top of the series quartz mangerite and charnockite.
(3) several large dykes and intrusions of overall monzonoritic characters, some of them varying in composition from norite to quartz mangerite /12/.

The fluorine content of 206 rocks is summarized in Table 1. The most striking feature is the relationship between the F and

Table 1

Fluorine and P_2O_5 contents of igneous rocks of the charnockitic family

	Fppm	P_2O_5%
Massif-type anorthosite		
anorthosite,leuconorite,norite	< 25	< 0.01
Bjerkreim-Sokndal lopolith		
Layered anorthosite,leuconorite and apatite-free norite	45-110	0.04-0.14
Layered apatite-bearing norite	1570-2800	1.90-3.30
Layered mangerite	350-800	0.4 - 0.9
Quartz mangerite(±olivine)	100-750	0.1 - 1.0
Amphibole charnockite	270-620	0.07- 0.3
Monzonoritic dykes and intrusions		
Antiperthitic norite (± quartz)	1370-2380	1.7 - 3.00
Monzonorite	1320-2470	1.5 - 3.1
Monzonite /Mangerite	800-1380	1.0 - 1.7
Quartz mangerite /charnockite	370-630	0.4 - 1.0

P_2O_5 contents of the rock, which is appeared to be linear in Fig.3. This clearly indicates that F is essentially contained in the mineral apatite $Ca_5(PO_4)_3(F,Cl,OH)$. This behaviour is well illustrated by the evolution in the Bjerkreim Sokndal massif, where apatite suddenly rises in the norites from very low content $(0.04-0.15\%)P_2O_5$ to the % level as soon as it becomes a liquidus mineral in process of fractional crystallization which is invoked to explain the massif /13,14/. Further on in the series of rocks, the apatite and F contents decrease progressively. A similar trend is also observed in the dykes and intrusions where the apatite content decreases with the evolution towards monzonite/mangerite and quartz mangerite. Again the crystallization of apatite can account for such a behaviour in successive liquids /12/. The average F/P_2O_5 ratio which can be deduced from the fig.3 is 785.10^{-4} which corresponds to a F content of the apatite of 3.4 %, a value which closely matches those measured by BAUMER et al. /15/ on apatite separated from Bjerkreim-Sokndal norites.
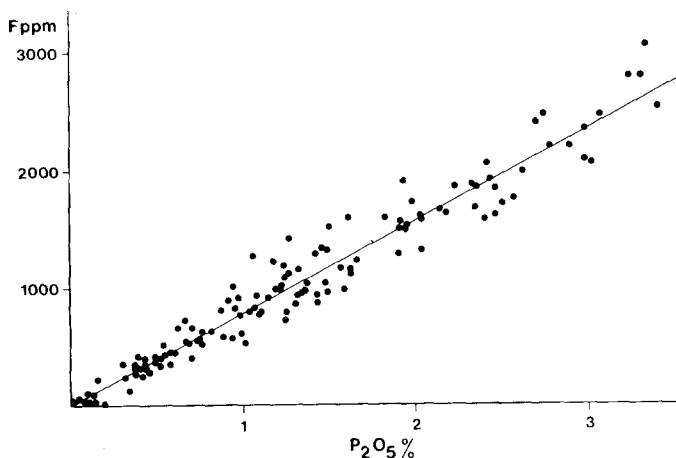

Fig. 3. F content vs. P_2O_5 in igneous rocks of the charnockitic family

The metamorphic rocks

A collection of rocks from the granulite facies terranes in which the igneous rocks were emplaced have been analysed. They essentially comprise metabasites, metapelites, granite-gneisses, meta-charnockites and augen-gneisses. The results are reported in Table 2. Fig.4 clearly shows that contrarily to the igneous rocks, the apatite content is not the sole factor which controls the F content of a rock.

In the metabasites, the presence of the hydroxyl-bearing minerals amphibole and biotite rises the F/P_2O_5 values from 785 10^{-4} in amphibole and biotite-free metabasites to $2800\ 10^{-4}$ and $11400\ 10^{-4}$ in biotite-bearing and amphibole-bearing metabasites

Table 2

Fluorine, P_2O_5 and K_2O contents of metamorphic rocks

|	n(1)	F (ppm)	P_2O_5 (%)	F/P_2O_5 10^{-4}	K_2O (%)
Metabasites					
Noritic	3	190–500	0.2–0.7	785	0.38
Amphibolite/amphibole-bearing noritic gneiss	5	1230–2900	0.1–0.3	11400	0.78
Biotite-bearing noritic-gneiss	4	1330–3570	0.8–1.2	2800	1.77
Metapelites					
Garnet-cordierite-sillimanite gneiss	3	∿30	∿0.04	∿750	3.7
Granite-gneisses	6	100–450	0.04–0.14	600–8200	5.31
Meta-charnockites	8	220–830	0.05–0.42	1050–4300	4.92
Augen-gneisses	2	1250	0.50	2500	3.06

(1) number of specimens
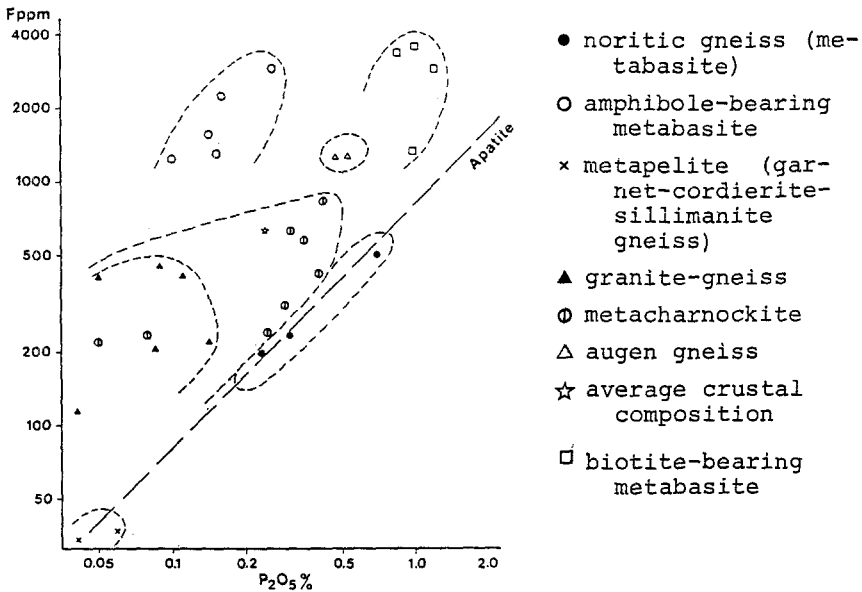
Fig. 4. F content versus P_2O_5 in metamorphic rocks around the Rogaland igneous bodies. (The dashed line gives the F/P_2O_5 ratio of the common apatite in igneous rocks)

respectively. It is generally admitted that the metabasites re-
sult from the metamorphism of basaltic igneous rocks. The F con-
tent of common basaltic rocks/16/ in the range of K_2O values re-
ported here (K_2O = 0.38 - 1.77) varies approximately from 300 ppm
to 800 ppm. The high values reported here (up to 3500 ppm) indi-
cate that the chemical system did not remain closed with respect
to F during· the metamorphism. Moreover, the systematic correla-
tion with the hydroxyl-minerals suggests that the F and H_2O were
associated in the fluid phase which was carried into the system
during the granulite facies metamorphism.

The metapelites are strongly depleted in F with respect to
their non metamorphic equivalents. Averages in the range of 500-
800 ppm F are currently reported for shales /17/. This strongly
suggests that F has been removed from the system together with
water during metamorphism.

The granite-gneisses and the metacharnockites show large and
overlapping domains of F-P_2O_5 variations. F appears to be con-
tained not only in apatite but also in biotite and/or amphibole,
which usually occur as minor constituents of the rocks. F is
depleted in granite-gneisses with regards to the average crustal
of 625 ppm and the average value adopted for granites (about
800 ppm) /1,2/. Again this feature can result from granulite
facies metamorphism. Some metamorphosed charnockites and augen-
gneisses can however be more F and P_2O_5 enriched than granite-
gneisses.

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